

0Dedicated to professor Gh. Marcu at his 80th anniversary

SPECTROSCOPIC AND MAGNETIC INVESTIGATIONS OF THE CHROMIUM(III) TUNGSTOARSENATE

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ABSTRACT. The sandwich-type tungstoarsenate complex $\text{Na}_6[\text{Cr}_4(\text{H}_2\text{O})_2](\text{AsW}_9\text{O}_{34})_2 \cdot 18\text{H}_2\text{O}$ (**Cr^{III}AsW₉**) was synthesized and investigated by elemental analysis, thermogravimetry, FT-IR, UV-VIS, EPR spectroscopy and magnetic susceptibility methods. The results suggest a sandwich-type structure in which two of the $[\text{AsW}_9\text{O}_{34}]^{9-}$ trilacunary Keggin fragments are connected by a Cr_4O_{16} group of four coplanar CrO_6 octahedra sharing edges.

The aim of this study consists in establishing the modifications that Cr^{III} ions make in the trivacant Keggin units, in determination of the local symmetry around the chromium ions and the identification of the nature of the chromium-chromium interactions.

Keywords: polyoxometalates, heteropolyoxometalates, chromium(III), tungstoarsenates

Introduction

Scientific interest in polyoxometalates is increasing worldwide, due to the enormous variety of structures of these compounds, often with unusual properties, rendering them useful candidates in medicinal applications and other fields such as nanomaterials, catalysis and magnetochemistry [1-4]. Although the mechanism of formation of polyoxometalates is commonly described as self-assembly, it is not well understood. In spite of this drawback, the synthesis of new compounds can be based on a rational synthetic approach and efficient control of the reaction path.

Lacunary polyoxometalates are usually synthesized from precursor ions by loss of one or more MO_6 octahedra [1, 5]. These lacunary polyoxometalates show an increased reactivity for metal ions and organometallic fragments, leading to the formation of a broad variety of complexes, in which the heteropolyanion framework remains unchanged. Taking into account the coordination requirements and the size of a given transition metal ion, the geometry of the reaction product can often be predicted.

Although polyoxometalate complexes of the trilacunary $[\text{PW}_9\text{O}_{34}]^{9-}$ with metal cations and organometallic fragments have been extensively investigated, there are relatively few papers concerning $[\text{AsW}_9\text{O}_{34}]^{9-}$ analogs [6-9].

Herein the synthesis and characterization of trilacunary $[\text{AsW}_9\text{O}_{34}]^{9-}$ (**AsW₉**) and $\text{Na}_6[\text{Cr}_4(\text{H}_2\text{O})_2](\text{AsW}_9\text{O}_{34})_2 \cdot 18\text{H}_2\text{O}$ (**CrAsW₉**) are reported. The complex was investigated using chemical and thermal analysis, UV-VIS, FT-IR and EPR spectra,

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as well as magnetic susceptibility measurements. The results suggest a sandwich-type structure similar to that reported by Knoth *et al.* [10], in which two of the **AsW₉** units are connected by a belt of four chromium atoms (Fig. 1).

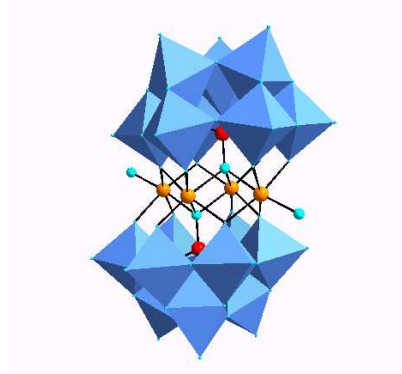


Fig. 1. Proposed structure of the $\text{Na}_6[\text{Cr}_4(\text{H}_2\text{O})_2](\text{AsW}_9\text{O}_{34})_2 \cdot 18\text{H}_2\text{O}$ polyoxometalate complex.

Experimental

1. Methods

Tungsten, chromium, sodium and arsenic were determined by atomic absorption. The water content was determined on the basis of thermal analysis performed using a METTLER-TGA/SDTA 851^eSTAR^eSoftware derivatograph. FT-IR spectra were recorded on a Jasco FT/IR 610 spectrophotometer in the 4000–400 cm^{-1} range, using KBr pellets. Electronic spectra in the visible range were performed in aqueous solutions on an ATI Unicam-UV-Visible spectrophotometer with Vision Software V 3.20. EPR spectra on powdered solids have been recorded at room temperature and 80 K at ca. 9.6 GHz (X-band) using a Bruker ESP 380 spectrometer. The magnetic susceptibility measurements were performed using a Faraday type balance in the temperature range of 77–273 K.

2. Materials

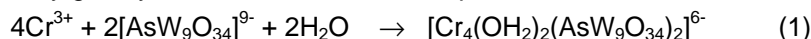
Reagent grade chemicals were used and all syntheses and studies were carried out in distilled water.

The sodium salt of the polyoxometalate ligand, $\text{Na}_8\text{H}[\text{AsW}_9\text{O}_{34}]$ (**AsW₉**) was prepared following the procedure described previously in the literature [11].

Synthesis of $\text{Na}_6[\text{Cr}_4(\text{OH}_2)_2(\text{AsW}_9\text{O}_{34})_2] \cdot 18\text{H}_2\text{O}$ $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (1.34 g, 3.094 mmol) was dissolved in water (10 ml) and added dropwise, while stirring, to a boiling aqueous solution (50 ml) of $\text{Na}_8\text{H}[\text{AsW}_9\text{O}_{34}] \cdot 11\text{H}_2\text{O}$ (5.5 g, 2.070 mmol). The slightly turbid final solution was boiled for 2h, its pH adjusted between 4.5 and 5.0 with 6M HCl, and filtered under suction. The filtrate was heated at 80°C, while stirring, until half of the volume remained. It was then cooled to room temperature. A few days later a green precipitate appeared. It was recrystallized from hot water, at pH= 6.0-6.5 and dried under vacuum over P_2O_5 . The yield was 2.3 g (60%). Anal. Calc. for $\text{H}_{40}\text{As}_2\text{Cr}_4\text{Na}_6\text{O}_{88}\text{W}_{18}$ (5776.95): As 2.80; Cr 4.00; Na 2.60; W 63.10. Found: As 2.85; Cr 3.96; Na 2.63; W 63.04. IR (polyoxometalate region, cm^{-1}): 955, 890, 839, 795, 734, 517, 472, 440.

Results and Discussions

The reaction of Cr^{III} with AsW_9 in water can be described by equation. (1). Isolation of the products as sodium salts and recrystallization from hot water, resulted in relatively good yields of the $\text{Cr}^{\text{III}}\text{AsW}_9$ complexes.



Elemental analysis of the final products are consistent with the suggested formula for $\text{Cr}^{\text{III}}\text{AsW}_9$.

Thermal study behavior of the new chromium (III) tungstoarsenate reveals that complex contain 18 crystallization water molecules and two coordination water molecules. For $\text{Cr}^{\text{III}}\text{AsW}_9$, two endothermic processes were observed between 120 and 260 °C (Fig. 2). These processes were assigned to water loss. The TG curves showed that the last process, corresponding to coordination water molecule loss, was the slowest. The exothermal process, appearing around 480°C on the DTA curve of complex, was assigned to the decomposition of polyoxometalate [12]. On the basis of these thermogravimetric studies, it can be thus concluded that $\text{Cr}^{\text{III}}\text{AsW}_9$ are thermally stable up to 480°C.

$\Delta m, \text{mg}$

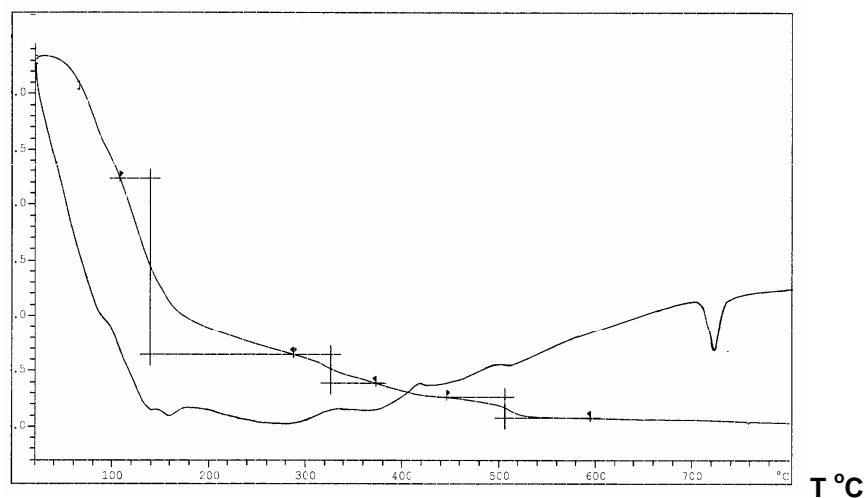


Fig. 2. Thermogravimetric and thermodifferential curves of $\text{Cr}^{\text{III}}\text{AsW}_9$.

Electronic Spectra

It have been registered the electronic UV and VIS spectra on aqueous solutions of the sodium salts of the polyoxometalates complex $\text{Cr}^{\text{III}}\text{AsW}_9$ and have been compared with this of the ligand AsW_9 .

The UV electronic spectra (Fig. 3) are characteristic to the polyoxometalates and similar to the ligand. [13,14] The higher energy band (ν_1) at $\sim 50000 \text{ cm}^{-1}$, due to the $d\pi\text{-}p\pi$ proper transitions from the $\text{W}=\text{O}_t$ (O_t -terminal oxygen atom) bonds, insignificantly shifted in the complex, compared to the ligand, which can be associated with the lack of involvement of the terminal oxygen atoms in the coordination of the cations of transitional metals.

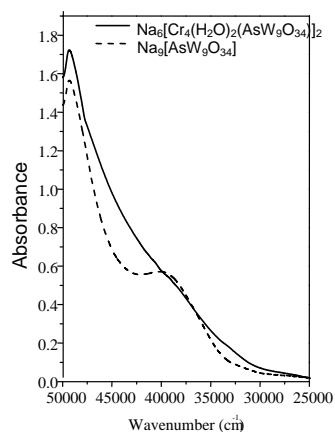


Fig. 3. UV spectra of the sodium salts of $\text{Cr}^{\text{III}}\text{AsW}_9$ (solid) and AsW_9 (dotted) obtained in $5 \times 10^{-5} \text{ mol} \cdot \text{l}^{-1}$ aqueous solution.

The lower energy band (ν_2) at $\sim 39000 \text{ cm}^{-1}$, due to the $d\pi\text{-}p\pi\text{-}d\pi$ electronic transitions from the tricentric $\text{W-O}_{\text{c,e}}\text{-W}$ ($\text{O}_{\text{c,e}}$ —bridging oxygens between two WO_6 octahedra sharing corner or edge respectively), bonds, with an expected absorption maximum in $40000\text{-}38000 \text{ cm}^{-1}$ range, in Cr^{III} complex spectrum, appearing as to shoulders in the spectrum, is due to the decrease of the symmetry as well as to the distortion of the WO_6 octahedra through complexation, which influences the electronic transfer from these bonds. [15]

Information about the local environment of $\text{Cr}(\text{III})$ ions has been obtained by means of d-d transitions from the visible electronic spectrum performed in aqueous solution. Two bands of the chromium complexes, at 16770 cm^{-1} and 21200 cm^{-1} are assigned to ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ (ν_1) and ${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$ (ν_2) transitions. The third band (${}^4\text{A}_{2g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$) expected in the UV domain is obscured by the charge-transfer and ligand-specific bands.

The first broad and unsplit band (ν_1) yields the $10D_q$ parameter, while the second (ν_2) is also broad and asymmetric. This can be explained by a small distortion from the ideal octahedral symmetry, because of the Jahn-Teller effect, spin-orbit coupling and the mixing of neighboring quartet-doublet states (${}^4\text{T}_{1g}$ and ${}^2\text{T}_{2g}$ or ${}^2\text{A}_{1g}$).

The position of the third band and the spectral parameters were calculated by the method proposed by Lever [16], using a value of 400 cm^{-1} for the interelectronic repulsion constant. The obtained values are: $D_q/B = 4.2$, $\nu_3/B = 88.6$, $\beta = 0.388$, $\nu_3 = 35286 \text{ cm}^{-1}$. The latter band (ν_3), assigned to a forbidden transition of two electrons, should have low intensity [17].

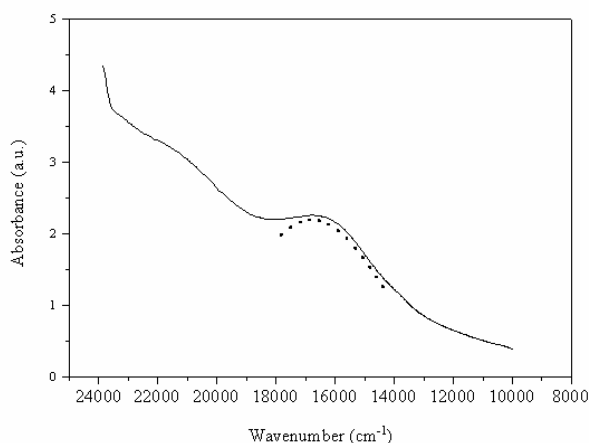


Fig.4. The visible electronic spectrum of the $\text{Cr}^{\text{III}}\text{AsW}_9$ complex in $5 \times 10^{-3} \text{ mol} \cdot \text{l}^{-1}$ aqueous solution. The Gaussian components are represented with dashed lines.

Vibrational Spectra

All antisymmetric frequencies bonds involving tungsten ions are shifted towards higher or lower frequencies ($1\text{--}18 \text{ cm}^{-1}$) in the complex spectrum compared to the ligand spectrum (Table 1).

The relative small shift of the $\nu_{\text{asym}}\text{W-O}_t$ vibration band from 945 cm^{-1} in the ligand spectrum to 950 cm^{-1} in complex spectrum is due to the fact that the terminal O_t atoms at the lacunary surface are not involved in the coordination of Cr^{III} ions [18]. The vibration frequencies of the As-O_i (O_i - internal oxygen atom) bonds are not observed at $\sim 820 \text{ cm}^{-1}$ overlaps that of $\text{W-O}_b\text{-W}$ (O_b – bridging oxygen atom) bonds. [18] Two vibration bands of tricentric $\text{W-O}_c\text{-W}$ bonds of the corner sharing WO_6 octahedra appear in spectrum of the ligand at 878 and 843 cm^{-1} , respectively, and in complex spectrum at 890 and 839 cm^{-1} , respectively, suggesting the nonequivalence of the $\text{W-O}_c\text{-W}$ bonds when linking octahedra from the equatorial and polar regions of the trilacunary fragments [18].

Two vibration bands of tricentric $\text{W-O}_e\text{-W}$ bonds of the edge-sharing WO_6 octahedra appear in the ligand spectrum at 795 and 752 cm^{-1} , respectively, suggesting that two nonequivalent bonds of this type are present. The complex spectrum shows two bands at 796 and 734 cm^{-1} too. [19]

TABEL 1.

FT-IR Data of the $\text{Cr}^{\text{III}}\text{AsW}_9$ complex and the AsW_9 ligand

Vibration band	$\nu \text{ (cm}^{-1}\text{)}$	
	AsW_9	$\text{Cr}^{\text{III}} \text{AsW}_9$
$\nu_{\text{as}}\text{W-O}_t$	945	950
$\nu_{\text{as}}\text{AsO}_i + \nu_{\text{as}}\text{W-O}_c\text{-W}$	878	890
$\nu_{\text{as}}\text{W-O}_c\text{-W}$	843	839
$\nu_{\text{as}}\text{W-O}_e\text{-W}$	795	795
	752	734

Magnetic measurements

The temperature dependence of the reciprocal molar susceptibility $1/\chi_m$ for the $\text{Cr}^{\text{III}}\text{--AsW}_9$ complex in the 77–273 K temperature range is presented in Fig. 5.

The effective magnetic moment obtained from the magnetic susceptibility data in the 77 – 273 K temperature range is $\mu_{\text{eff}} = 10.66 \mu_B$. The value of Curie-Weiss temperature $\theta = -6.1$ K, indicates the presence of antiferromagnetic coupling between the Cr^{III} ions.

These measurements, together with the informations obtained from EPR spectroscopy, led to the establishment of intra- and intermolecular metal-metal interactions .

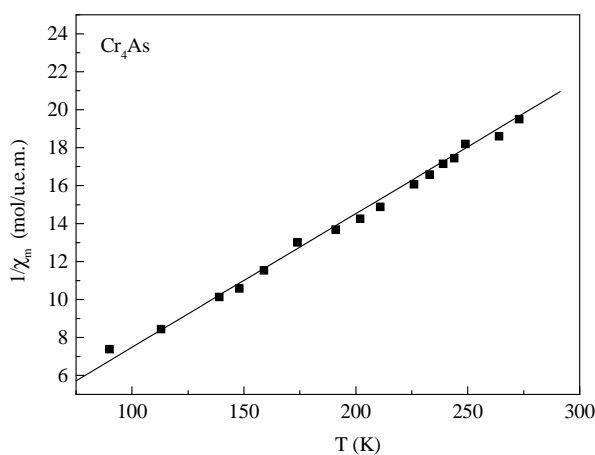


Fig. 5. Variation of reciprocal molar susceptibility of the $\text{Cr}^{\text{III}}\text{AsW}_9$ complex with respect to temperature. Solid line represents the best fit of the experimental data with a Curie-Weiss behavior.

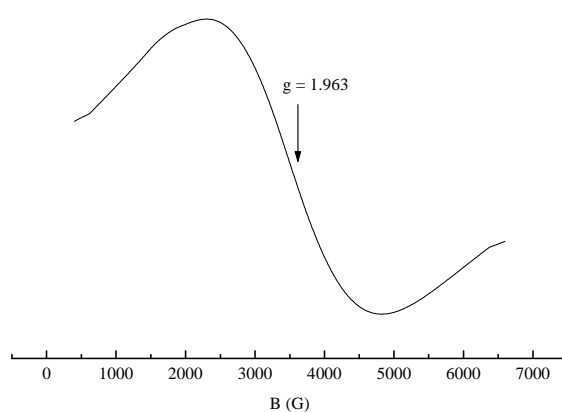


Fig. 6. EPR Spectrum of the $\text{Cr}^{\text{III}}\text{AsW}_9$

EPR Spectrum

The polycrystalline EPR spectrum of the Cr complex obtained at 80 K contains a single large ≈ 2495 G pseudo-isotropic signal centered at $g=1.963$. The line width of the signal indicates the presence of the coupling between the chromium ions; the almost isotropic shape of this is due to an O_h symmetry around the chromium (III) ions. The shape of this signal is not modified at 293 K. By raising the temperature, the line width of signal decreases, which indicates the presence of small Cr(III)-Cr(III) super-exchange interactions (Fig. 6). [20]

Conclusions

The results of the performed investigations revealed that the chromium complex of the AsW_9 trilacunary polyoxometalate was prepared. A sandwich-type structure, similar to the structure of the other complexes reported by Knoth *et. al.*, [10] (Fig. 1) is inferred from the experimental results. The coordination of the chromium (III) ions in the lacunary region of the Keggin units results from the shift of the $\nu_{asym}(W-O_{c,e}-W)$ stretching frequencies in the FT-IR spectrum of the complex compared to the ligand spectrum.

Every metal ion is surrounded by six oxygen atoms in a distorted O_h symmetry and has a $d_{x^2-y^2}$ orbital as ground state. The almost isotropic shape form of the signal from EPR spectrum registered on the $Cr^{III}AsW_9$ is due to an O_h symmetry around the Cr^{III} .

The magnetic susceptibility measurements in the 77–273 K temperature range have indicated the presence of antiferromagnetically coupled Cr^{III} ions.

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